

# On the inequivalence of statistical ensembles

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We investigate the relation between various statistical ensembles of finite systems. If ensembles differ at the level of fluctuations of the order parameter, we show that the equations of states can present major differences. A sufficient condition for this inequivalence to survive at the thermodynamical limit is worked out. If energy consists in a kinetic and a potential part, the microcanonical ensemble does not converge towards the canonical ensemble when the partial heat capacities per particle fulfill the relation  $c_k^{-1} + c_p^{-1} < 0$ .

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In most textbooks the equivalence between the different statistical ensembles is demonstrated at the thermodynamical limit through the Van Hove theorem [1]. Indeed ensembles differ at the level of fluctuations which are generally believed to induce small corrections in finite systems and to become negligible at the limit of infinite systems.

In this paper we will show that this might not be always the case. For finite systems, two ensembles which put different constraints on the fluctuations of the order parameter lead to qualitatively different equations of states close to a first order phase transition. As an example the microcanonical heat capacity may diverge to become negative while the canonical one remains always positive and finite [2, 3]. Such inequivalences may survive at the thermodynamical limit for systems involving long range forces [4, 5]. Looking at the general properties of the order parameter distribution a sufficient condition for this behavior to show up can be explicitly worked out.

Let us first concentrate on finite systems. For simplicity we will consider the microcanonical and the canonical ensemble characterized by the energy  $E$  and the temperature  $\beta^{-1}$  respectively, but our discussion is valid for any couple of conjugated extensive and intensive variables.

The microcanonical ensemble is characterized by the level density  $W(E)$  and the entropy  $S = \log W$ . The caloric curve is then  $T^{-1} = \partial_E S$ . The canonical partition sum is the Laplace transform of  $W$ :  $Z_\beta = \int dE W \exp(-\beta E)$ . In this article we will assume that the partition sum converges; this is not always the case [6] and indeed the impossibility to normalize the distribution  $W \exp(-\beta E)$  is already a known case of ensemble inequivalence.

In finite systems, the canonical ensemble differs from the microcanonical one since it does not correspond to a unique energy but to a distribution  $P_\beta(E) = \exp(S(E) - \beta E - \log Z_\beta)$ . If  $P_\beta$  has a single maximum the average energy  $\langle E \rangle_\beta = -\partial_\beta \ln Z_\beta$  can also be computed using a saddle point approximation around the most probable energy  $\bar{E}_\beta$

$$\langle E \rangle_\beta = \int dE E P_\beta(E) = \int dE E e^{-\frac{(E - \bar{E}_\beta)^2}{2C}} g_\beta(E - \bar{E}) \quad (1)$$

with  $g_\beta(x) = c_0 + c_3 x^3 + c_4 x^4 + \dots$ . If  $P_\beta$  is symmetric,  $\langle E \rangle_\beta = \bar{E}_\beta$ . The definition of saddle implies

$$T^{-1} \equiv \partial_E S(\bar{E}_\beta) = \beta \quad (2)$$

meaning that the microcanonical caloric curve  $T(\bar{E})$  exactly coincides with the canonical one  $\beta^{-1}(\langle E \rangle)$ . However in a finite system the distribution may be not symmetric so that the two curves can be shifted:  $\langle E \rangle_\beta = \bar{E}_\beta + \delta_\beta$ , where  $\delta_\beta = \int dx x \exp(-x^2/2C) \tilde{g}_\beta(x) = 3c_3 \sqrt{2\pi C^5} + \dots$  with  $\tilde{g}_\beta$  the series of the odd terms of  $g_\beta$ . However, the shift  $\delta$  is in most cases small so that when  $P_\beta$  has a unique maximum the ensembles are almost equivalent even for a finite system.

A more interesting situation occurs in first order phase transitions where  $P_\beta$  has a characteristic bimodal shape [7, 8, 9] with two maxima  $\bar{E}_\beta^{(1)}$ ,  $\bar{E}_\beta^{(2)}$  that can be associated with the two phases and a minimum  $\bar{E}^{(0)}$ . These three solutions of Eq.(2) imply a backbending for the microcanonical caloric curve. A single saddle point approximation is not valid in this case; however it is always possible to write  $P_\beta = m_\beta^{(1)} P_\beta^{(1)} + m_\beta^{(2)} P_\beta^{(2)}$  with  $P_\beta^{(i)}$  mono-modal normalized probability distribution peaked at  $\bar{E}_\beta^{(i)}$ . The canonical mean energy is then the weighted average of the two energies

$$\langle E \rangle_\beta = \tilde{m}_\beta^{(1)} \bar{E}_\beta^{(1)} + \tilde{m}_\beta^{(2)} \bar{E}_\beta^{(2)} \quad (3)$$

with  $\tilde{m}_\beta^{(i)} = m_\beta^{(i)} \int dE P_\beta^{(i)}(E) E / \bar{E}_\beta^{(i)} \simeq m_\beta^{(i)}$ , the last equality holding for symmetric distributions  $P_\beta^{(i)}$ . As before correcting terms depending on the skewness  $c_3^{(i)}$  can be easily derived.

Since only one mean energy is associated with a given temperature  $\beta^{-1}$ , the canonical caloric curve is

monotonous, meaning that in the first order phase transition region the two ensembles are not equivalent

If instead of looking at the average  $\langle E \rangle_\beta$  we look at the most probable energy  $\bar{E}_\beta$ , this (unusual) canonical caloric curve is identical to the microcanonical one (see eq. (2)) up to the transition temperature  $\beta_t^{-1}$  for which the two components of  $P_\beta(E)$  have the same height. At this point the most probable energy jumps from the low to the high energy branch of the microcanonical caloric curve. The canonical curve is still monotonic and presents a plateau at  $\beta_t^{-1}$  which is equivalent to the Maxwell construction since

$$S(\bar{E}_\beta^{(2)}) - S(\bar{E}_\beta^{(1)}) = \int_{\bar{E}_\beta^{(1)}}^{\bar{E}_\beta^{(2)}} \frac{dE}{T} = \beta \left( \bar{E}_\beta^{(2)} - \bar{E}_\beta^{(1)} \right) \quad (4)$$

The question arises whether this violation of ensemble equivalence survives towards the thermodynamical limit. This limit can be expressed as the fact that the thermodynamical potentials per particle converge when the number of particles  $N$  goes to infinity :  $f_{N,\beta} = \beta^{-1} \log Z_\beta/N \rightarrow \bar{f}_\beta$  and  $s_N(e) = S(E)/N \rightarrow \bar{s}(e)$  where  $e = E/N$ . Let us also introduce the reduced probability  $p_{N,\beta}(e) = (P_\beta(N, E))^{1/N}$  which then converges towards an asymptotic distribution  $p_{N,\beta}(e) \rightarrow \bar{p}_\beta(e)$  where  $\bar{p}_\beta(e) = \exp(\bar{s}(e) - \beta e + \bar{f}_\beta)$ . Since  $P_\beta(N, E) \approx (\bar{p}_\beta(e))^N$  one can see that when  $\bar{p}_\beta(e)$  is normal the relative energy fluctuation in  $P_\beta(N, E)$  is suppressed by a factor  $1/\sqrt{N}$ . At the thermodynamical limit  $P_\beta$  reduces to a  $\delta$ -function and the ensemble equivalence is recovered.

The situation is more complicated in the case of a first order phase transition, i.e. for a bimodal  $p_{N,\beta}(e)$ . As before, let us introduce  $\beta_{N,t}^{-1}$  the temperature for which the two maxima of  $p_{N,\beta}(e)$  have the same height. For a first order phase transition  $\beta_{N,t}^{-1}$  converges to a fixed point  $\bar{\beta}_t^{-1}$  as well as the two maximum energies  $e_{N,\beta}^{(i)} \rightarrow \bar{e}_\beta^{(i)}$ . For all temperature lower (higher) than  $\bar{\beta}_t^{-1}$  only the low (high) energy peak will survive at the thermodynamical limit since the difference of the two maximum probabilities will be raised to the power  $N$ . Therefore, below  $\bar{e}_\beta^{(1)}$  and above  $\bar{e}_\beta^{(2)}$  the canonical caloric curve coincides with the microcanonical one in the thermodynamical limit. In the canonical ensemble the temperature  $\bar{\beta}_t^{-1}$  corresponds to a discontinuity in the state energy irrespectively of the behavior of the entropy between  $\bar{e}_\beta^{(1)}$  and  $\bar{e}_\beta^{(2)}$ .

The microcanonical caloric curve in the phase transition region may either converge towards the Maxwell construction or keep a backbending behavior, since a negative heat capacity system can be thermodynamically stable even in the thermodynamical limit if it is isolated [10]. This point has been recently made in somewhat different words by Leyvraz and Ruffo[11]. Examples of a backbending behavior at the thermodynamical limit have been reported for a model many-body interaction taken as a functional of the hypergeometric radius in ref.[4]

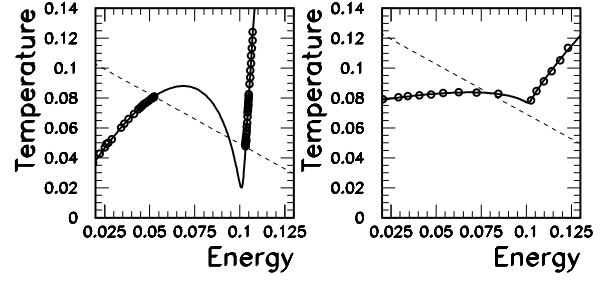


FIG. 1: Temperature as a function of the potential energy  $E_2$  (full lines) and of the kinetic energy  $E - E_2$  (dashed lines) for two model equation of states of classical systems showing a first order phase transition. Symbols: temperatures extracted from the most probable kinetic energy thermometer from eq.(5).

and for the long range Ising model [5]. This can be understood as a general effect of long range interactions for which the topological anomaly leading to the convex intruder in the entropy is not cured by increasing the number of particles[5, 12]. Conversely, for short range interactions [3] the backbending is a surface effect which should disappear at the thermodynamical limit. This is the case for the microcanonical model of fragmentation of atomic clusters[13] and for the lattice gas model with fluctuating volume[14]. The interphase surface entropy goes to zero as  $N \rightarrow \infty$  in these models leading to a linear increase of the entropy in agreement with the canonical predictions. From these examples, we can conclude that in the coexistence region the microcanonical equation of states may remain different from the canonical one even at the thermodynamical limit if the involved phenomena are not reduced to short range effects.

An especially interesting situation occurs for hamiltonians containing a kinetic energy contribution: if the kinetic heat capacity is large enough we will now show that the microcanonical curve presents at the thermodynamical limit a temperature jump in complete disagreement with the canonical ensemble.

Let us consider a finite system for which the hamiltonian can be separated into two components  $E = E_1 + E_2$ , that are statistically independent ( $W(E_1, E_2) = W_1(E_1)W_2(E_2)$ ) and such that the associated degrees of freedom scale in the same way with the number of particles; we will also consider the case where  $S_1 = \log W_1$  has no anomaly while  $S_2 = \log W_2$  presents a convex intruder which is preserved at the thermodynamical limit. Typical examples of  $E_1$  are given by the kinetic energy for a classical system with velocity independent interactions or other similar one body operators [5].

The probability to get a partial energy  $E_1$  when the total energy is  $E$  is given by

$$P_E(E_1) = \exp(S_1(E_1) + S_2(E - E_1) - S(E)) \quad (5)$$

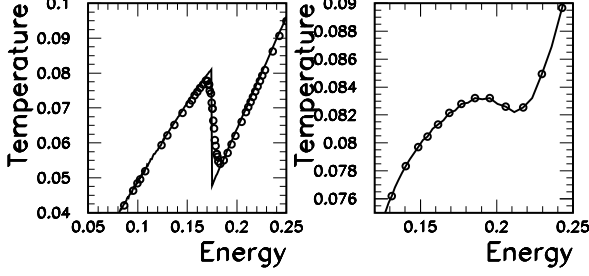


FIG. 2: Symbols: total caloric curves obtained with the potential and kinetic equations of state of figure 1. Lines: thermodynamical limit from a (double) saddle point approximation of the partial energy microcanonical distributions.

The extremum of  $P_E(E_1)$  is obtained for the partitioning of the total energy  $E$  between the kinetic and potential components that equalizes the two partial temperatures  $\bar{T} = \partial_{E_1} S_1(\bar{E}_1) = \partial_{E_2} S_2(E - \bar{E}_1)$ . If  $\bar{E}_1$  is unique,  $P_E(E_1)$  is mono-modal and we can use a saddle point approximation around this solution to compute the entropy  $S(E) = \int_{-\infty}^E dE_1 \exp(S_1(E_1) + S_2(E - E_1))$ . At the lowest order this leads to the microcanonical temperature of the global system  $\partial_E S(E) = \bar{T}^{-1}$  meaning that the most probable partial energy  $\bar{E}_1$  acts as a microcanonical thermometer. If  $\bar{E}_1$  is always unique, the kinetic thermometer in the backbending region will follow the whole decrease of temperature as the total energy increases. Therefore, the total caloric curve will present the same anomaly as the potential one.

If conversely the partial energy distribution is double humped [15], then the equality of the partial temperatures admits three solutions one of them  $\bar{E}_1^{(0)}$  being a minimum. At this point the partial heat capacities  $C_1^{-1} = -\bar{T}^2 \partial_{E_1}^2 S_1(\bar{E}_1^{(0)})$  and  $C_2^{-1} = -\bar{T}^2 \partial_{E_2}^2 S_2(E - \bar{E}_1^{(0)})$  fulfill the relation

$$C_1^{-1} + C_2^{-1} < 0 \quad (6)$$

This happens when the potential heat capacity is negative and the kinetic energy has a sufficient number of degrees of freedom ( $C_1 > -C_2$ ) to act as an approximate heat bath: the partial energy distribution  $P_E(E_1)$  in the microcanonical ensemble is then bimodal as the total energy distribution  $P_\beta(E)$  in the canonical ensemble. In this case the microcanonical temperature is given by a weighted average of the two estimations from the two maxima of the kinetic energy distribution

$$T = \partial_E S(E) = \frac{\bar{P}^{(1)} \sigma^{(1)} / \bar{T}^{(1)} + \bar{P}^{(2)} \sigma^{(2)} / \bar{T}^{(2)}}{\bar{P}^{(1)} \sigma^{(1)} + \bar{P}^{(2)} \sigma^{(2)}} \quad (7)$$

where  $\bar{T}^{(i)} = T_1(\bar{E}_1^{(i)})$  are the kinetic temperatures calculated at the two maxima,  $\bar{P}^{(i)} = P_E(\bar{E}_1^{(i)})$  are the probabilities of the two peaks and  $\sigma^{(i)}$  their widths. At the

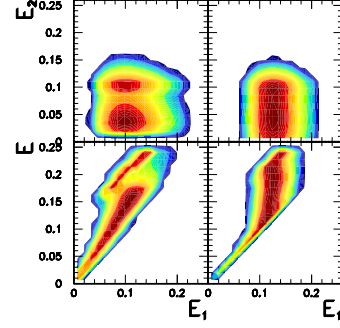


FIG. 3: Canonical event distributions in the potential versus kinetic energy plane (upper part) and total versus kinetic energy plane (lower part) at the transition temperature for the two model equations of state of figure 1.

thermodynamical limit eq.(6) reads  $c_1^{-1} + c_2^{-1} < 0$ , with  $c = \lim_{N \rightarrow \infty} C/N$ . If this condition is fulfilled the probability distribution  $P_\beta(E)$  presents two maxima for all finite sizes and only the highest peak survives at  $N = \infty$ . Let  $E_t$  be the energy at which  $P_{E_t}(\bar{E}^{(1)}) = P_{E_t}(\bar{E}^{(2)})$ . Because of the zero principle eq.(7) at the thermodynamical limit the caloric curve will follow the high (low) energy maximum of  $P_E(E_1)$  for all energies below (above)  $E_t$ ; there will be a temperature jump at the transition energy  $E_t$ .

Let us illustrate the above results with two examples for a classical gas of interacting particles. For the kinetic energy contribution we have  $S_1(E) = c_1 \ln(E/N)^N$  with a constant kinetic heat capacity per particle  $c_1 = 3/2$ . For the potential part we will take two polynomial parametrizations of the interaction caloric curve presenting a back bending which are displayed in figure 1. If the decrease of the partial temperature  $T_2(E_2)$  is steeper than  $-2/3$  (left part) [4] eq.(6) is verified and the kinetic caloric curve  $T_1(E - E_1)$  (dashed line) crosses the potential one  $T_2(E_2)$  (full line) in three different points for all values of the total energy lying inside the coexistence region. The resulting caloric curve for the whole system is shown in figure 2 (symbols) together with the thermodynamical limit (lines) evaluated from the double saddle point approximation (7). In this case one observes a temperature jump at the transition energy while if the temperature decrease is smoother (right part of figures 1 and 2) the shape of the interaction caloric curve is preserved at the thermodynamical limit.

The occurrence of a temperature jump in the thermodynamical limit is easily spotted by looking at the bidimensional canonical event distribution  $P_\beta(E_1, E_2)$  in the partial energies plane. This density of states is just the product of the independent kinetic and potential canonical probabilities as shown in the upper part of figure 3 for the two model equation of states of figure 1 at the transition temperature  $\beta = \beta_t$ . In order to discuss the microcanonical ensemble one has to introduce the total energy  $E = E_1 + E_2$ . Thus we can look at the canonical

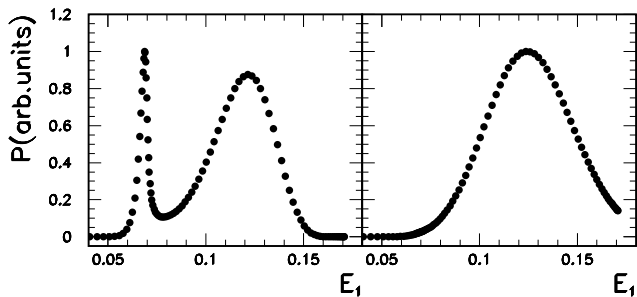


FIG. 4: Microcanonical kinetic energy distributions inside the coexistence region for the two model equations of state of figure 1.

distribution as a function of  $E$  and  $E_1$

$$P_\beta(E, E_1) \propto \exp S_1(E_1) \exp S_2(E - E_1) \exp(-\beta E) \quad (8)$$

which is shown in the lower part of figure 3. The deformation of the event distribution induced by the microcanonical constraint does not cause a topological difference between our two model cases; this explains why both converge to the Maxwell construction for  $N \rightarrow \infty$  in the canonical ensemble. If we now study the microcanonical ensemble we have to look at constant energy cuts of  $P_\beta(E, E_1)$  leading to the microcanonical distribution  $P_E(E_1)$  within a normalization constant. If the anomaly in the potential equation of state is sufficiently important, the distortion of events is such that one can still see the two phases coexist even after a sorting in energy. Figure 4 shows two cuts of the lower part of figure 3 at an energy close to the transition energy. In the system which does not present a temperature jump the partial

energy distribution is normal, while the two peaks of the system violating ensemble equivalence can be interpreted as the precursors of phases [9]. This can also be seen from the most probable kinetic temperature (symbols in the left part of figure 1) which makes a sudden jump at the transition energy.

In conclusion, in this paper we have analyzed the distribution of observable quantities related to the order parameter in finite systems undergoing a first order phase transition. This phenomenon is uniquely signed by a bimodality of the probability distribution in the intensive ensemble where the Lagrange parameter associated to the considered observable is fixed. In such a physical situation the different statistical ensembles are not in general equivalent even at the thermodynamical limit. In finite systems, the order parameters (e.g. energy in the considered examples) have an average value which varies smoothly while the most probable value makes a jump as a function of the associated Lagrange multiplier (e.g. temperature) in the intensive (e.g. canonical) ensemble. In the corresponding extensive (e.g. microcanonical) ensemble the corresponding equation of states (e.g. the caloric curve) presents a back bending. In infinite systems, this inequivalence between statistical ensembles may remain. We have shown that a generic behavior of the extensive ensemble can be a discontinuity in the associated intensive variable at a given value of the fixed extensive variable. The condition for this ensemble inequivalence can be explicitly worked out in a wide range of physical systems. In particular, microcanonical caloric curves present a temperature jump at the thermodynamical limit if the negative heat capacity is sufficiently small in absolute value for the kinetic energy to play the role of a heat bath.

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